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(54) Title: IMPROVED PROCESSABILITY OF METALLOCENE-CATALYZED POLYOLEFINS

(57) Abstract

Metallocene-catalyzed polyolefins exhibit a tendency to increase motor loads and torque when extruded, due to their relative shear insensitivity. The use of a solid solvent combined with the linear polyolefin can reduce motor loads and torque to improve processability. The solid solvent chosen should leave the physical properties of an extrusion fabricated article substantially unaltered when compared to the properties of the linear polyolefin itself. The linear polyolefin will have a M_w/M_n less than 2.8. The solid solvent will have: a disassociation temperature (T_{di}) below the processing temperature of the combination of linear polyolefin and solid solvent, an association temperature (T_a) above the crystallization temperature of the linear polyolefin; a solubility index from 15 to 20 $MPa^{1/2}$, a M_n from 250 to 5000; an extractibility (in combination with the polyolefin) in n-hexane at 50 °C below 5.5 weight percent for the total blend, a degradation temperature in excess of 300 °C, and a refractive index within ± 10% of the refractive index of the linear polyolefin.

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TITLE: **Improved Processability of Metallocene-Catalyzed Polyolefins**

TECHNICAL FIELD

This invention relates generally to materials added to metallocene-catalyzed narrow molecular weight polyolefin polymers made with metallocene catalyst systems to improve their melt processing properties. More specifically, this invention relates to solid solvents to improve the melt processability of metallocene-catalyzed polyolefins and polyolefin blends containing one or more metallocene-catalyzed polyolefins, while physical properties of articles fabricated with these polyolefins and solvents are substantially the same as those of articles fabricated from the linear polyolefin itself.

BACKGROUND

Advances in polymer synthesis technology have often brought with them changes in processing of the polymers subsequent to polymerization. For example, when a low pressure gas-phase or solution reactor produced, traditional Ziegler-Natta catalyzed, linear low density polyethylene (LLDPE) process was widely commercialized in the late 1970's and 1980's, substantially all such polymers produced were less shear sensitive in the melt phase than, for instance, free radical polymerized polyolefins, the latter having been widely used prior to the LLDPE introduction. The LLDPE polymer's higher melt viscosity at typical processing conditions made the then existing extrusion and molding equipment less efficient as a polymer pumping apparatus, for instance as measured by pounds per hour per inch of die (lb./hr/in of die) (kg/hr/cm of die) when used to process linear low density Ziegler-Natta catalyzed polyolefin polymers.

The introduction of metallocene-catalyzed linear polymers has, in certain instances, once again brought similar melt processing difficulties, probably due at least in part to the comparatively narrow molecular weight distribution and narrow composition distribution of these metallocene-catalyzed materials when compared for example to traditional Ziegler-Natta catalyzed polyolefin polymers, solution polymerized mono-cyclopentadienyl catalyzed polyolefins, or especially to free radical initiated polyolefins. Due to the newness of the metallocene-catalyzed polyolefin polymers and their relatively low current commercial volume of sales, fabricators and converters of polyolefin polymers have not been compelled to push the processing envelope of these polymers. As metallocene-catalyzed polyolefin polymers reach

commercially significant sales and use, their relative difficulty of processing of certain of these metallocene-catalyzed polymers will become more important as converters of these resins attempt to maximize the output on a given machine while using these new polymers.

Polyolefins (hereinafter "metallocene-catalyzed polyolefins") made from metallocene based catalyst systems (which include mono-cyclopentadienyl and bis(cyclopentadienyl) metallocene catalyst systems as described in U.S. Patents 5,026,798 and 5,324,800 incorporated herein by reference for purposes of U.S. patent practice) generally display a narrow molecular weight distribution (MWD) (M_w/M_n) generally less than 4, preferably less than 3. These polymers show remarkably improved physical properties compared with, for instance, traditional Ziegler-Natta catalyzed polyolefin polymers, due in part to their relatively narrow compostion distribution and narrow molecular weight distribution. However, in certain instances, particularly with polyolefins prepared from bis(cyclopentadienyl) catalyst systems, their narrow molecular weight distribution also gives them a generally higher viscosity at melt processing temperatures, that is generally higher than that of mono-cyclopentadienyl catalyzed polymers, traditional Ziegler-Natta catalyzed linear polymers, or free radical polymerized polyolefins. This viscosity difference, combined with a lower melt phase shear sensitivity of these metallocene-catalyzed polymers than certain other metallocene, traditional Ziegler-Natta catalyzed polyolefin polymers and free radical polymerized polyolefins, leads to more difficult melt phase processing or in other words, higher motor loads, higher extruder back-pressures, and potentially lower maximum specific output. Such higher torque and motor loads mean that often a given extruder's output may be lowered because the energy or horsepower of the extruder may not be sufficient to pump as much of a more viscous polymer. Alternatively, more energy may be used to pump the same amount of polymer (at a constant output based on weight/unit of die circumference/unit of time) if the machine is not power limited.

In the past there have been numerous attempts, many of them successful, to improve the processability of various kinds of polymers. These attempts have included adding lubricants, or plasticizers, use of other viscosity reduction techniques, and other methods of improving processing. However, along with improving melt processability, many of these solutions have had deleterious effects on other important aspects of polymer melt processing, fabrication, and fabricated articles made from these polymers. Some examples of such detrimental effects include that the materials intended to improve processability tend to reduce physical properties, and that others have drawbacks such as increasing solvent extractables (limited for food law compliance).

Others have an unacceptable level of volatility causing unacceptable smoking or plate-out in melt processing operations. Another problem common to many previous solutions was that while lowering power requirements, motor load and/or torque, output decreased, as measured by the specific output (kg/hr/cm of die).

To improve polymer melt phase processability, some solutions have been offered. Chung in the Journal of Applied Polymer Science suggests the concept of a solid solvent utilizing a low molecular weight crystalline material (LMC) as a processing aid. A LMC is purported to become a solvent for the polymer at high processing temperatures reducing the melt viscosity and thus enhancing processability, but to become a non-solvent for the polymer at low use temperature precipitating out of the polymer without adversely affecting the properties. This document suggests using acetanilide as a solid solvent for polystyrene and two ABA-type block copolymers containing polystyrene end blocks.

EP 0 279 573 A2 suggests that the melt viscosity of vinylidene chloride polymers is purportedly reduced by introducing a solid solvent such as dimethyl sulfone into the polymer. The sulfone may be compatible with vinylidene chloride polymers at a processing temperature above the solid solvent melting point and will reduce the melt viscosity and improve processing of the vinylidene chloride polymer. Upon cooling below the solid solvent melting point, the solid solvent is said to become micro dispersed in the vinylidene chloride polymer with little or no solid solvent remaining dissolved in the vinylidene chloride polymer.

EP 0 324 264 A2 suggests that the extrudability of linear polymers of ethylene such as low density copolymers of ethylene of a C4 to C10 olefins (LLDPE) into thin films is improved by adding small amounts, for example, of 0.02 to 2 weight percent ethylene vinyl polymer to reduce melt fracture, head pressure and to obtain having excellent anti-blocking characteristics. Optionally, diatomaceous earth is added to further reduce blocking.

EP 0 308 090 A2 suggests that head pressure and extruder torque in the extrusion of linear ethylene polymers such as linear low density polyethylene (LLDPE) are reduced by adding a small amount (less than 3 weight percent) of a thermoplastic polyamide polymer. Films extruded from the blend purportedly exhibit better surface appearance by reduction of melt fracture.

EP 0 308 089 A2 suggests that head pressure and extruder torque in the extrusion of linear ethylene polymers such as linear low density polyethylene (LLDPE) are purportedly reduced by adding a small amount (less than 5 weight percent) of a

thermoplastic polyurethane. Films extruded from the blend are said to exhibit better surface appearance by reduction of melt fracture.

There is a commercial a need therefore for a material that may generally lower extrusion power requirements, lower extruder back pressure, improve the melt processability of metallocene-catalyzed polymers on a specific output basis, and may have a substantially neutral or improvement effect on most fabricated article physical properties.

SUMMARY

I have discovered that combining metallocene-catalyzed polyolefins with a solid solvent can provide advantages in melt processing of metallocene-catalyzed polyolefins. The advantages include, but are not limited to; lower extruder torque, lower extruder back-pressures, lower power requirements and/or improved maximum outputs at substantially the same specific extruder output, and with generally little smoking and/or plate-out. Additionally, these advantages can be realized generally without loss of physical properties of an article fabricated from the combination. I have thus found that the above discussed disadvantages associated with metallocene-catalyzed polyolefins can generally be solved by the material combinations of various embodiments of my invention.

When a solid solvent is used in a metallocene-catalyzed polyolefin, the result is a combination which has a polyolefin or polyolefins (majority component) selected from a group consisting of polyethylene, polypropylene, ethylene homopolymers, ethylene-alpha-olefin copolymers, ethylene alpha-olefin terpolymers, propylene homopolymers, propylene-ethylene copolymers, propylene-alpha-olefin copolymers or terpolymers and mixtures (combinations) and blends thereof, where the polyolefin is made from the group of catalysts or initiators consisting of a metallocene or single site catalyzed polymerization products, a traditional Ziegler-Natta catalyzed system, and a Chromium based catalyst system. However, the majority component can also contain an additional polymer or polymers. The majority component has a density in the range of from 0.85 to 0.97 g/cc preferably in the range of from 0.86 to 0.96 g/cc.

The combination may also include in the range of 0.5 to 10 parts per hundred parts of the majority component, generally a metallocene-catalyzed polyolefin. As referred to in the present application, solid solvent means a material which is dispersed in the polymer in an associated state (crystal, micel, or cluster, for example) at temperatures below the processing temperature of the polymer. The solid solvent may dissociate somewhat below the (melt) processing temperature of the majority

component and should have sufficiently low molecular weight to enhance extrudability, but sufficiently high molecular weight to prevent substantial screw slippage (in an extruder), smoking, or fuming during melt processing, solvent extractability (food law compliance), and plate-out. The solid solvent should preferably reassociate during or somewhat before solidification of a fabricated article based on the combination, to form a separate phase within the polymer article.

The minority or solid solvent component has: (a) a disassociation temperature (T_{di}) at or below the processing temperature of the blend; (b) an association temperature (T_a) equal to or above the crystallization temperature of the polyolefin; (c) a solubility index in the range of from 15 to 20 $(MPa)^{1/2}$; (d) optionally a degree of crystallinity exceeding 80%; (e) a viscosity not exceeding 2000 MPa at 170°C; (f) an extractability in n-hexane at 50°C not exceeding 5.5 weight percent based on the total weight of the combination with the majority component; (g) a degradation temperature in excess of 250°C; and (h) a refractive index within ±10% of the polyolefin majority component.

These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description and appended claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Introduction

One embodiment of the present invention is directed to a combination of a polyolefin and a solid solvent, as well as articles fabricated based on this combination. These polyolefin compositions have improved melt processability properties which make them unique and particularly well suited for use in most melt processing operations used for fabrication of metallocene-catalyzed polyolefins.

Following is a detailed description of certain preferred metallocene-catalyzed polyolefins and solid solvents within the scope of various embodiments of my invention, preferred methods of combining the polyolefins and solid solvents, and preferred applications of these combinations. Those skilled in the art will appreciate that numerous modifications to these preferred embodiments can be made without departing from the scope of the invention. For example, while the properties of the combinations are exemplified in films and film extruders with which they are made, the combination will find use in numerous other fabricated articles. To the extent that this description is specific, this is solely for the purpose of illustrating preferred embodiments, and should not be taken as limiting.

The ability to improve the melt processability of such metallocene-catalyzed polyolefins without generally negatively affecting the physical properties of fabricated articles, has been heretofore unobtainable.

The metallocene-catalyzed polyolefin/solid solvent combinations of various embodiments of the present invention will contain at least these two components. Such combinations can be achieved by schemes including but not limited to, melt compounding, dry blending, or other schemes which will be well known to those of ordinary skill in the art.

The use of headings in the application are intended to aid the reader and no other significance or limitation is intended.

The Majority Component

The majority component of the combination of the present invention is generally a melt processable polymer or polymer blend selected from the group consisting of: polyethylene, polypropylene, copolymers and terpolymers of ethylene and propylene, ethylene propylene rubber, ethylene propylene diene monomer rubber (EPDM), styrene isoprene styrene, styrene butadiene styrene, and combinations thereof. These polymers are becoming available commercially and may be prepared or polymerized by metallocene and/or single site catalyst systems, however other constituents of the "majority" component may be polyolefins catalyzed or initiated with other types of catalysts or initiators or other types of catalyst mixtures. Examples of free radical, high pressure polyethylenes and ethylene copolymers include but are not limited to homopolymer polyethylene, ethylene vinyl acetate, ethylene ethyl acrylate, ethylene methyl acrylate, ethylene n-butyl acrylate, ethylene acrylic acid, ethylene methacrylic acid, ionomers of the acid co or terpolymers, combinations thereof and the like.

The majority component polyolefin may be an ethylene homopolymer or an ethylene-alpha-olefin copolymer where the polymer contains one or more alpha-olefins. The alpha-olefins will have from 3 to 20 carbon atoms. The polyolefin may also be a polypropylene, either a homopolymer polypropylene or a copolymer or terpolymer of propylene and ethylene and/or an alpha-olefin having 4 to 20 carbon atoms. The preferred alpha-olefins in either the polyethylene or the polypropylene copolymers or terpolymers, are olefins having 4 to 8 carbon atoms. Non-limiting examples of these alpha-olefins are butene-1, 4-methyl pentene-1, hexene-1, and octene-1. The use of terpolymers and tetrapolymers of the ethylene or propylene using alpha-olefins are also

contemplated, as are blends of the polyolefin with other polyolefin copolymers or other thermoplastics.

While I anticipate that the primary benefit, or the most pronounced effect of the solid solvent on processability, will be evidenced with bis(cyclopentadienyl) metallocene-catalyzed polyolefins, the effect of these solid solvents will also be discernible in traditional Ziegler-Natta catalyzed, chromium catalyzed polyolefins, free radical initiated polyolefins, mono-cyclopentadienyl metallocene-catalyzed polyolefins and combinations thereof, as well, albeit, to a generally lesser degree. The majority component polyolefins may be produced in a gas phase fluidized bed reactor, stirred bed reactors, solution reactor, slurry or bulk reactors of the tank or loop type.

The use or inclusion into either the majority component, or for instance into the article fabricated from the combination of majority components and solid solvent include additives, such as for instance antioxidants, acid neutralizers, antiozonants, UV inhibitors or absorbers, colors, fillers, combinations thereof and the like are also contemplated.

Ethylene Polymers

When the polyolefin is a copolymer or terpolymer of ethylene and an alpha-olefin, the alpha-olefin or alpha-olefins are present in the ethylene copolymer in the range of from 0.2 to 20 mole percent based on the total moles of copolymer, preferably in the range of from 0.5 to 15 mole percent, more preferably in the range of from 1 to 10 mole percent. The melt index of the ethylene copolymers will be in the range of from 0.01 dg/min to 100 dg/min, preferably in the range of from 0.25 to 10 dg/min, more preferably 0.5 dg/min to 10 dg/min (as measured by ASTM D 1238 condition E 190° C 2.16 kg). The density of the polymers is in the range of from 0.85 to 0.96 g/cc, preferably in the range of from 0.89 to 0.93 g/cc. The choice of a specific density and melt index will be driven mainly by the end use article property requirements. The molecular weight distribution of the ethylene-alpha-olefin copolymers will generally be below 2.8 (M_w/M_n) preferably below 2.5. The composition breadth distribution index (CDBI) of the ethylene-alpha-olefin copolymer is greater than 50%, preferably more than 65. A description of methods of determining both CDBI may be found in copending application USSN 08/230,661 which is incorporated herein by reference for purposes of US patent practice.

Propylene Polymers

The propylene polymers contemplated are also catalyzed by metallocene based catalysts systems. These polymers may be propylene homopolymers or propylene or copolymers or terpolymers. A propylene copolymer, terpolymer, or tetrapolymer may also be propylene where the monomers may be selected from the group consisting of ethylene and/or alpha-olefins where the alpha-olefins have a carbon number in the range of 4 to 20, more preferably the carbon number is from 4 to 10, most preferably from 4 to 8. Comonomer or comonomers will be present in the copolymer in the range of from 0.2 to 8 mole percent based on the total mole of the copolymer, preferably from 0.5 to 6 mole percent, more preferably from 1 to 3 mole percent. The melt flow rate of any of these propylene polymers will be in the range of from 0.1 to 5000 g/10 min. (as measured by ASTM D-1238 Condition L (230°C/2.6 Kg)).

If the propylene copolymer is intended for use in a film or sheeting application, the melt flow rate is more preferably in the range of from 0.5 to 10 g/10 min. If the end use or the melt process used to convert the propylene polymer resin into a useful fabricated article is fiber spinning or extrusion, the melt flow rate is preferably in the range of from 10 to 3000 g/10 min, more preferably in the range of from 100 to 1500 g/10 min. The composition distribution of the propylene copolymers is generally narrow. The molecular weight distribution of the propylene copolymers demonstrated by the Mw/Mn is in the range of up to 2.8, preferably up to 2.5, and most preferably to 2.

Solid Solvents

The solid solvents contemplated by the present invention include a broad range of materials that can most generally be described as those materials whose molecules disassociate in the melt, where the solid solvent will act as a viscosity modifier, but then will reassociate (through crystallization, micel formation, ionic bonding and the like) before or simultaneously with the recrystallization of the majority component polyolefin.

The solid solvent will have a disassociation temperature (T_{di}) less than the normal processing temperature or melt processing temperature of the majority component, preferably more than 10° C below the melt processing temperature, more preferably more than 20° C below the melt processing temperature.

The association temperature (T_a) of the solid solvent will be equal to or greater than crystallization temperature of the majority component, preferably 10° C greater than the crystallization temperature, preferably 20° C greater than the crystallization

temperature. It will be understood by those of ordinary skill in the art that regardless of the crystallization temperature of the majority component, the crystallization temperature of the solid solvent will preferably be at or above the crystallization temperature of the majority component polyolefin. The T_a and the T_{di} can be measured utilizing techniques well known to those of ordinary skill in the art, such as Dynamic Mechanical Thermal Analysis (DMTA), differential scanning calorimeter (DSC), or hot stage microscopy.

If the solid solvent is generally non-crystalline in nature, before or simultaneously with the crystallization temperature of the majority component, the solid solvent will reassociate with the majority component. Likewise the material will disassociate at a temperature of less than the typical processing temperatures for the majority component polyolefin.

In general the solid solvent (either crystalline, non-crystalline or partially crystalline) selected will act as a viscosity modifier in the melt phase of the majority component polyolefin and will be disassociated from the polyolefin. On the other hand, after the solid solvent has reassociated and the majority component has crystallized, the solid solvent will be sufficiently reassociated with the majority component that the extractability of the combination of solid solvent, majority component, and additives will not be greater than 5.5 weight percent, preferably less than 4 weight percent, more preferably less than 3 weight percent, most preferably less than 2.6 weight percent(of the total combination) in n-hexane, as measured by a standard test of the US Food and Drug Administration noted 21 CFR § 177.1520.

Additionally, the solid solvent should reassociate with the majority component such that the physical properties of an article made from the combination should not have substantially lower values than that of the majority component without the solid solvent added.

Solid Solvents may be selected from the group consisting of C_{20} to C_{70} hydrocarbons, monofunctional C_{20} to C_{70} hydrocarbons, and multifunctional C_{20} to C_{70} hydrocarbons, wherein said functionality is selected from the group consisting of alcohols, acids, esters, sulfonates, aldehydes, ketones, ethers acid amides, amines and combinations thereof. Additionally, the solid solvent should have a number average molecular weight (M_n) in the range of from 250 to 5000. Non-limiting examples of such solid solvent materials are shown below in table I. Each of the materials are available from at least one commercial source, and one of those sources is indicated in the table. Additionally Chemical Abstracts numbers (CAS#), are included for clarity.

TABLE 1

Name (Alternative Name)	Carbon Number	Melting Point (C)	Company Code	Cas#
ALCOHOLS				
1-Eicoanol (arachidyl alcohol)	20	64	PNB	629-96-9
Benzopinacole (tetraphenylethylene glycol)	26	184	KNG	464-72-2
1-Triacontanol	30	93	AUS	593-50-0
ACIDS				
Eicosanoic acid (arachidic acid)	20	75	POI	506-30-9
Docosanoic acid (behenic acid)	22	80	UNC	112-85-6
cis-13-Docosenoic acid (erucic acid)	22	3	UNC	112-86-7
ESTERS				
Stearyl acetate (octadecyl acetate)	20	34	PEN	822-23-1
Tristearyl citrate	57		CSIUS	7775-50-0
Glycerol tristearate (tristearin)	57	73	CILUS	555-43-1
SULFONATES				
Sodium octaecylaminonaphthalenesulfonate	28		MPR	30536-61-9
KETONES				
2,2,2,-Triphenylacetophenone	26	182	KNG	466-37-5
3,4-di(decyloxy)acetophenone	28		JNSBE	118468-33-0
Dioctadecylketone	37		KNKUS	2123-20-8
ALDEHYDES				
3,4-Di(octyloxy)benzaldhyde	21		JNSBE	131525-50-3
3,4-Di(decyloxy)benzaldehyde	27	63	JNSBE	118468-34-1
ETHERS				
Methyl trityl ether	20	96	PNB	596-31-6
Didodecyl ether	24	32	TCI	4542-57-8
Dioctadecyl ether	36	62	TCI	6297-03-6
AMIDES				
Eruoamide	22	79	UNC	112-84-5
Octadecyl stearamide	36	94	HMK	13276-08-9
Erucyl eruamide	44		HMK	87075-61-4
AMINES				
4-Tetradecylanillne	20	46	PNB	91323-12-5
4-(Triphenylmethyl)aniline	25	255	PNB	22948-06-7
Tri(tridecyl)amine	39		SHX	5910-77-0

Key for Table 1:

Company Code	Company Name
AUS	AccuStandard Inc.
CILUS	Cambridge Isotope Labs
CSIUS	Chem Service Inc.
HMK	Witco Corp.
JNSBE	Janssen Chimica
KNG	King's Laboratory, Inc.
KNKUS	K & K Labs
MPR	Molecular Probes Inc.
PEN	Penta Manufacturing Co.
PNB	Pfaltz & Bauer Inc.
POL	Polyester Corp.
SHX	Witco Corp.
TCI	T. C. I. America Inc.
UNC	Unichema North America

The solubility index (ρ) of the solid solvent [Polymer Handbook - J. Brandrup/E. H. Immergut (Wiley Interscience Publications, 1989, pg. VII - 519 to pg. VII-559)] should be 16.5 $MPa^{1/2}$, preferably in the range of from 15 to 20, more preferably in the range of from 15 to 19.5 $MPa^{1/2}$. It will be understood that the solubility index is a measure of compatibility with the polyolefin material.

The degradation temperature or T_d of the solid solvent should be greater than 250° C, preferably greater than 275° C and more preferably greater than 300° C. It will be well understood by those of ordinary skill in the art that the degradation temperature of the solid solvent should be chosen such that degradation during normal extrusion conditions of the majority component polyolefin be avoided. To determine a satisfactory degradation temperature limit for a solid solvent, weight loss may be kept below 2.5 weight percent, preferably below 1.5, more preferably below 1 weight percent. Such weight loss may be determined by for instance Thermo-Gravimetric Analysis (TGA).

The refractive index of the polyolefin/solid solvent combination should be as close as possible to the refractive index of the majority component polyolefin preferably in the range of ± 10% of the refractive index of the majority component, where the clarity of the end product of the melt processable polyolefin is of importance.

The volatility of the solids solvent should be minimal. Those of ordinary skill in the art will appreciate that the volatility should be kept at or below the level of volatility, at normal processing temperatures, of the majority component melt

processable polyolefin to avoid smoking, die build-up, and buildup on other parts around the die and extrusion zone.

Where required, the solid solvent should preferably be food law compliant.

Melt processes contemplated

Extrusion and molding are two broad categories of melt processing that take in substantially all of the shear and heat conversion processes encountered by polyethylenes or polypropylenes. Extruded products can be made into films having a thickness in the range of from 5 microns to 200 microns or a sheet having a thickness in the range of from 200 micron to 4000 microns, or fibers having a broad range of fiber deniers. In the case of films, the films may be blown films or cast films. These processes will be known to those of ordinary skill in the art. Also contemplated are extrusion blow molding and injection molding melt processing techniques.

Polyolefin Uses

Uses for polyolefin/solid solvent melt processable blends include: blown and cast films, oriented films, fibers (melt blown and spun bonded), fabrics made from said fibers, sheets and molded articles (injection molding, compression molding, extrusion blow molding, and extrusion stretch blow molding).

Such extruded materials find use in trash bags, can liners, t-shirt bags, stretch films, heavy duty shipping sacks, retail bags, meat, cheese and produce packaging, snack foods packaging, food containers, diaper back sheets, diaper liners, diaper fillers, medical drapes and gowns, medical devices (e.g. syringes, IV tubing, and the like.), bottles, and pails.

Examples

Example 1

An ethylene butene copolymer (EXACT® 3028, available from Exxon Chemical Company) made utilizing a metallocene catalyst is blown into a mono-layer film on a in the blown film application on a 2.5 in (64 mm) Egan extruder (24:1 L:D) with a 60 mil (1.5 mm) die gap. The same resin was used for all three Samples. The gauge of the film made from the polymer is 1.25 mils (31.75 microns). The butene copolymer has a density of approximately 0.90 g/cc and a melt index of a nominal 1.2 dg/min. Sample 1 (control) is Exact 3028 extruded without additives, save for anti-oxidants, acid neutralizers, and the like, and Viton® A to substantially eliminate melt fracture. In runs 2 and 3, respectively the additives included are 500 ppm Viton® A.

(Viton A can be obtained from E. I. DuPont and is one of a family of fluoroelastomers) Such fluoroelastomers are generally useful as processing aids that generally act to eliminate melt fracture.

Sample 2 has 500 ppm Viton A, and 4 weight percent of a solid solvent, a low molecular weight polypropylene wax PP 230, (available from Hoechst Celanese). Sample 3 has 500 ppm Viton A and 7.5 weight percent of LD-200.48 (a nominal 8 dg/min melt index free radical initiated low density polyethylene material with 0.917 g/cc density from Exxon Chemical Company). Sample 3 represents previously suggested materials (highly branched LDPE) to improve processability.

As can be seen from Table II, the control (Sample 1) exhibited a motor load (KVA) of 12.6 compared to 10.2 and 12.4 KVA respectively for Samples 2 and 3.

Back pressure was 24.4 MPa for Sample 1, versus 21, and 23.1 MPa respectively for samples 2 and 3.

The Table II data would indicate that the additives of samples 2 and 3 improved processability to varying degrees. However, Sample 2 showed substantially more improvement than either Sample 1 or 3 in all the above comparisions.

In reviewing the film property data Table III referring to the same sets of samples, inventive Sample 2 shows dramatic property improvements in Elmendorf tear, puncture force, and puncture energy when compared to Sample 1. Specifically over 18% improvement in both MD and TD tear values over the reference (Sample 1). While in puncture force the inventive Sample 2 is over 23% greater than Sample 1, and in puncture energy the improvement of Sample 2 is greater than 50% over Sample 1 (control).

Example 2

A blend of propylene-ethylene and propylene-hexene copolymers are extruded into a film. The motor load in KVA for the two controls (propylene-ethylene and propylene-hexene copolymers) when compared to those of the same additives as added in Example 1 are diminished at least by 10%. The same order of magnitude reduction is seen in back pressure.

Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. For example, other melt processing methods are contemplated such as for example, compounding and molding. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained herein.

TABLE II

GRADE	UNITS	Sample 1 REFER EXACT 3028	Sample 2 +4%PP230	Sample 3 +7.5%LD200
COMONOMER	—	BUTENE	BUTENE	BUTENE
DENSITY	G/CC	0.9	0.9	0.902
MELT INDEX	G/10'	1.2	—	—
MOTOR LOAD @ 65 RPM	AMPS	44.5	36.2	44
	KVA	12.6	10.2	12.4
BACK PRESSURE	MPa	24.4	21.0	23.1
*FLH	m	0.76	0.69	0.76
MELT TEMPERATURE	degC	209	207	207
MOTOR LOAD (AMPS)	% OF REF	100	81.3	98.9
BACK PRESSURE	% OF REF	100	86.1	94.8
BUBBLE STABILITY	MPM	42.7	42.7	54.9

*FLH = frost line height

TABLE III

BLOWN FILM PROPERTIES
(2.5" EGAN / 60 mil DIE GAP)

GRADE	UNITS		Sample 1 REFER. EXACT 3028	Sample 2 +4%PP230	Sample 3 +7.5% LD200
COMONOMER	—		BUTENE	BUTENE	BUTENE
DENSITY	G/CC		0.9	0.9	0.902
MELT INDEX	G/10'		1.2	—	—
GAUGE AVERAGE	Micron		31.9	31.9	31.9
1% SECANT MODULUS	MPa	MD	75.7	77.9	82.2
	MPa	TD	78.7	71.4	82.5
TENSILE @ YIELD	MPa	MD	4.69	4.65	5.39
	MPa	TD	4.41	4.36	4.75
ELONGATION @ YIELD	%	MD	8.02	7.84	7.98
	%	TD	7.59	8.12	7.87
ELONGATION @ BREAK	%	MD	529	539	564
	%	TD	650	666	684
ULTIMATE TENSILE	MPa	MD	60.9	61.3	50.8
	MPa	TD	49.9	50.1	50.9
ELMENDORF TEAR	N/mm	MD	48.3	57.1	44.0
	N/mm	TD	73.0	79.1	69.9
DART IMPACT	N/mm		>557	>557	>557
PUNCTURE FORCE	N/mm		1183	1461	1260
PUNCTURE ENERGY	J/mm		96	147	110
HAZE	%		1.8	2.9	1.3
GLOSS	%		83.7	79	87.2

CLAIMS:

I claim:

1. A polyolefin composition comprising:

i) a majority component, said majority component including: a metallocene-catalyzed polyolefin selected from the group consisting of ethylene homopolymers, ethylene α-olefin copolymers, polypropylene homopolymers, polypropylene copolymers and combinations thereof; and

ii) a solid solvent present in the range of from 0.5 to 10 parts per hundred parts of said majority component wherein said solid solvent has:

a) a T_{di} below the processing temperature of the blend, preferably 20° C or more below the processing temperature of the majority component;

b) a T_a point at least at the crystallization temperature of said polyolefin, preferably 20° C or more higher than the crystallization temperature of said majority component;

c) a solubility index in the range of from 15 to 20 $MPa^{1/2}$;

d) an extractability in n-hexane at 50°C temperature not exceeding 5.5 weight percent based on the total weight of the composition;

e) a degradation temperature in excess of 250°C;

f) a refractive index within ±10% of said polyolefin; and wherein said solid solvent is selected from the group consisting of, monofunctional C_{20} to C_{70} hydrocarbons, and multifunctional C_{20} to C_{70} hydrocarbons, wherein said functionality is selected from the group consisting of alcohols, acids, esters, sulfonates, aldehydes, ketones, ethers, acidamides, amines and combinations thereof, preferably 1 wherein said solid solvent is a metal salt of C_{20} to C_{70} organic acids.

2. The polyolefin composition of claim 1 wherein said solid solvent is one of a crystalline material or a semi-crystalline material, with a melting point lower than the processing temperature of said polyolefin.

3. A blend comprising:

a) a polyolefin selected from the group consisting of polyethylene, polypropylene, ethylene-alpha-olefin copolymers, propylene-ethylene

copolymers, propylene-alpha-olefin copolymers and combinations thereof; and

b) a solid solvent present in said blend in the range of 0.5 to 10 parts per hundred parts of said polyolefin, and

wherein said polyolefin has a Mw/Mn less than 2.8; and

wherein said solid solvent is selected from the group consisting of, monofunctional C_{20} to C_{70} hydrocarbons, and multifunctional C_{20} to C_{70} hydrocarbons, wherein said functionality is selected from the group consisting of alcohols, acids, esters, sulfonates, aldehydes, ketones, ethers, acidamides, amines and combinations thereof.

4. A polyethylene composition comprising:

i) a majority component, said majority component including:

a metallocene-catalyzed polyethylene selected from the group consisting of ethylene homopolymers, ethylene α-olefin copolymers, and combinations thereof, wherein said majority component has a density in the range of from 0.89 to 0.93 g/cc, wherein said α-olefins, if present are present in the range of from 0.2 to 20 mole percent based on the total moles of said copolymer, wherein said alpha-olefin, if present is selected from the group consisting of butene-1, hexene-1, 4-methyl pentene-1, octene-1, and mixtures thereof ; and

ii) a solid solvent present in the range of from 0.5 to 10 parts per hundred parts of said majority component, wherein said solid solvent has:

a) a T_{di} below the processing temperature of the blend;

b) a T_s point at least at the crystallization temperature of said polyolefin;

c) a solubility index in the range of from 15 to 20 MPa$^{1/2}$;

d) an extractability in n-hexane at 50°C temperature not exceeding 5.5 weight percent based on the total weight of the composition;

e) a degradation temperature in excess of 300°C;

f) a refractive index within ±10% of said polyethylene,

wherein said solid solvent is selected from the group consisting of, monofunctional C_{20} to C_{70} hydrocarbons, multifunctional C_{20} to C_{70} hydrocarbons, and a metal salt of a C_{20} to C_{70} organic acid and combinations thereof, wherein said functionality is selected from the

group consisting of alcohols, acids, esters, sulfonates, aldehydes, ketones, ethers, acidamides, amines.

5. A polyolefin composition comprising:

i) a majority component, said majority component including: a metallocene-catalyzed polyolefin selected from the group consisting of ethylene homopolymers, ethylene α-olefin copolymers, polypropylene homopolymers, polypropylene copolymers and combinations thereof; and

ii) a solid solvent present in the range of from 0.5 to 4 parts per hundred parts of said majority component wherein said solid solvent has:

a) a T_{di} below the processing temperature of the blend;

b) a T_a point at least at the crystallization temperature of said polyolefin;

c) a solubility index in the range of from 15 to 20 $MPa^{1/2}$;

d) an extractability in n-hexane at 50°C temperature not exceeding 5.5 weight percent based on the total weight of the composition;

e) a degradation temperature in excess of 250°C;

f) a refractive index within ±10% of said polyolefin; and wherein said solid solvent is a C_{20} to C_{70} hydrocarbon.

6. A blend comprising:

a) a polyolefin selected from the group consisting of polyethylene, polypropylene, ethylene-alpha-olefin copolymers, propylene-ethylene copolymers, propylene-alpha-olefin copolymers and combinations thereof; and

b) a solid solvent present in said blend in the range of 0.5 to 4 parts per hundred parts of said polyolefin, and

wherein said polyolefin has a Mw/Mn less than 2.8; and

wherein said solid solvent is a C_{20} to C_{70} hydrocarbon.

7. The blend of claims 3 or 6 wherein said polyolefin is made in the presence of a metallocene catalyst.

8. The blend as recited in claims or 6 wherein said polyethylene is a polyethylene having a density in the range from 0.915 to 0.960 g/cc.

9. The blend as recited in claims 3 or 6 wherein the polyethylene is an ethylene-alpha-olefin copolymer wherein the alpha-olefin is selected from the group consisting of propene-1, butene-1, hexene-1, 4-methyl pentene-1, octene-1, and mixtures thereof said alpha-olefin being present in said ethylene copolymer in the range of from 0.2 to 20 mole percent based on the total moles of the copolymer.

10. The blend as recited in claims 3 or 6 wherein the polyethylene is one of a homopolymer, copolymer, or terpolymer of ethylene having a density in the range of from 0.85 to 0.96 g/cc.

11. The blend as recited in claims 3 or 6 wherein the polyethylene is one of a homopolymer, copolymer, or terpolymer of ethylene having a density in the range of from 0.89 to 0.93 g/cc.

12. The blend of claims 3 or 6 wherein said polypropylene copolymer is a copolymer of propylene and a comonomer selected from the group consisting of ethylene, butene-1, 4-methyl pentene-1, hexene-1, octene-1 and mixtures thereof, wherein said comonomers are present in said propylene copolymer in the range of 0.2 to 6 mole percent based on the total moles of the propylene copolymer.

13. Use of the blend as recited in claims 5 or 8 in a film.

14. Use of the blend as recited in claims 5 or 8 in a fiber.

15. Use of the blend as recited in claim 5 or 8 in a molded article.

16. Use of the blend as recited in claims 5 or 8 in a fabric.

INTERNATIONAL SEARCH REPORT

Interr ...al Application No
PCT/US 96/05039

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L23/04 C08L23/10 //(C08L23/04,91:06),(C08L23/10,91:06)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 282 882 (HOECHST AG) 21 September 1988 see claims ---	1-16
A	EP,A,0 277 750 (MITSUI PETROCHEMICAL IND) 10 August 1988 see claims -----	1-16

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 96/05039

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